

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Method of preparing Fuel Cell Catalysts

We, AMERICAN CYANAMID COMPANY, a corporation organised under the laws of the State of Maine, United States of America, of Berdan Avenue, Township of Wayne, State of New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a method for preparing catalytic electrodes of enhanced performance eminently suitable for use in a variety of fuel cells, such as hydrogen-oxygen, hydrogen-air, hydrazine-oxygen and ammonia-oxygen fuel cells. More particularly, the invention relates to the preparation of a catalytic electrode comprising a reduced noble metal. The term "noble metal" is used herein to refer to the Group VIII noble metals, viz. the metals ruthenium, osmium, rhodium, iridium, palladium and platinum.

As is known, noble metal catalysts, such as platinum, palladium and rhodium, have been employed in electrode structures for use in either alkaline or acid fuel cells. Usually, the noble metal catalysts are initially formed by chemical reduction utilizing, for instance, alkali metal borohydrides. The reduced metal is deposited on an electrically conductive filler, such as carbon. The resultant mixture is next waterproofed and spread on a metallic screen to form an electrode which is widely used in the fuel cell art. However, electrodes so prepared perform rather poorly with increasing densities and attendant decrease in voltages. As a consequence, continued efforts have been made to provide improved fuel cell electrodes which enable both increased current densities and increased voltages to be obtained.

We have now unexpectedly found that electrodes prepared from a silane-reduced noble metal compound are enhanced to an extent hitherto unknown. Surprisingly, there is obtained a reduced noble metal whose crystallite

size, obtained by X-ray analysis, averages between 20 Å and 35 Å, with the result that the reduced noble metal exhibits markedly high activity when utilized in fuel cell electrodes, thus enabling fuel cells of improved performance to be provided. This result is in contradistinction to that obtained by the use of a typical alkali metal borohydride reduction which results in a noble metal catalyst whose average crystallite size is usually not less than 65 Å.

According to the process of the invention, a silane-reduced noble metal catalyst which is suitable for use as an effective electrode component can be prepared in an inexpensive and straightforward manner. This is accomplished by the reduction of the noble metal compound, such as chloroplatinic acid, rhodium chloride or mixtures thereof, as well as their corresponding bromo or iodo derivatives, in an alcoholic solvent with a di- or tri-substituted silane containing a Si—H group. The reduction takes place preferably at temperatures from 20°C. to 100°C., while agitating in the presence of an electrically conductive filler. The latter is added prior to reduction, so that the particles of noble metal which form as soon as reduction occurs, will precipitate on or coat the conductive filler.

To the resultant catalyst mixture as prepared, there may next be added a binder-waterproofing agent in aqueous emulsion form comprising, for instance, polytetrafluoroethylene, polychlorotrifluoroethylene or polyethylene. A spreadable paste is formed which can be spread on a suitable surface. One such surface is glass which may, upon drying, permit the formation of a strippable sheet. Alternatively, and more desirably, the paste can be spread on a suitable screen or grid. Illustrative of the latter are stainless steel, tantalum, nickel, and asbestos paper.

In general, any alcoholic solvent can be employed during the reduction, provided the solvent maintains the substituted silane in

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solution. Exemplary of such solvents are, for instance, methanol, ethanol, propanol and butanol.

As illustrative of the di- and tri-substituted silane employed in the process of the invention, there can be mentioned the following: dimethyl silane, diethyl silane, triethyl silane, triisopropyl silane, tributyl silane, diphenyl silane, ditolyl silane, triphenyl silane, tribenzyl silane and triethoxy silane. In each of the aforementioned silanes which are soluble in alcoholic solvents, there is present a Si—H group, whereby reduction can be effected.

An electrode containing the hereinabove described silane-reduced noble metal can be cut to any desired shape for use in a fuel cell. As is known, there is employed in a fuel cell a matrix or membrane which separates the electrodes. In order to obtain fuel cells of improved performance it is not necessary that both the electrodes should have been prepared in accordance with the process of this invention.

The matrix component of the fuel cell is saturated with either base or acid electrolyte. Ordinary filter paper, asbestos fiber paper as well as polymeric membranes containing commercially available ion exchange materials can be used. The latter material may also be used in either a leached or water-equilibrated state. For illustrative purposes, ordinary filter paper which is saturated with either 5N or 8N potassium hydroxide can be employed herein as the matrix or electrode-separating membrane.

The invention is illustrated by the Examples which follow. Unless otherwise stated, the parts are by weight.

EXAMPLE 1

In a suitable reaction vessel are suspended 9 parts of graphite (prepared as a by-product

of calcium cyanamide manufacture) in 300 parts of ethyl alcohol. There is then added 2.5 parts of chloroplatinic acid which readily dissolves in alcohol. The resultant mixture is heated to 75°C., there is slowly added 3 parts of diphenyl silane previously diluted with 75 parts of ethyl alcohol. Reduction of the chloroplatinic acid takes place. Reduced platinum metal is deposited on the graphite. With continued agitation, the mixture is held at between 75°C. and 80°C. for at least 30 minutes. The temperature is then reduced and the contents of the reaction vessel are washed in a suitable container with ethanol and then with water. The respective liquids are decanted and the solid material comprising platinum deposited on carbon is then dried. Resultant dried material is analyzed and found to contain 10% platinum on carbon. This metal is admixed with an aqueous dispersion of polytetrafluoroethylene binder-water-proofing agent and spread on a 100 mesh (U.S. Standard) nickel screen, whereby an electrode sheet containing one milligram of platinum per square centimeter of electrode surface area is prepared. As determined by X-ray analysis, the crystallite size of the platinum present in the electrode is found to average 30 Å.

A one inch disc cut from the above-prepared electrode sheet is placed on the hydrogen side of a hydrogen-oxygen fuel cell. As the oxygen electrode, there is employed a platinum black electrode having a ten milligram per square centimeter loading.

Comparative data over a wide range of current densities at 70°C. utilizing the above-described electrode and one prepared by sodium borohydride reduction following the procedure hereinabove described, but substituting sodium borohydride in lieu of diphenyl silane, are shown in Table I below.

TABLE I

Electrode	Current Density (ma/cm ²) as		
	Hydrogen Electrode at		
	.85	.80	.75 volts
NaBH ₄ -reduced:1 mg Pt/cm ²	60	100	135
Silane-reduced:1 mg Pt/cm ²	130	180	230

EXAMPLE 2

The procedure of Example 1 is repeated in every detail except that the reducing agent employed in preparing the electrode is triethyl silane. Substantially the same performance as noted in Table I is obtained.

EXAMPLE 3

The procedure of Example 1 is repeated in every detail except that propanol as the solvent and tributyl silane as the reducing agent are employed in lieu of ethanol and diphenyl silane, respectively. An electrode is

prepared demonstrating substantially the same fuel cell performance when so incorporated therein.

EXAMPLE 4

5 Again the procedure of Example 1 is followed in every detail except that instead of 2.5 parts of chloroplatinic acid there is employed a mixture of 1.25 parts of chloroplatinic acid and 1.25 parts of rhodium chloride and the resulting electrode containing 0.5

milligram of platinum and 0.5 milligram of rhodium per square centimeter is tested in the same manner as the electrode of Example 1. Unexpectedly, the test results are markedly superior when comparing the electrode of the present invention with one made by employing an equal amount of platinum and rhodium obtained by a reduction utilizing conventional sodium borohydride reduction techniques. The performance of each cell is summarized in Table II below.

TABLE II

Electrode	Current Density (ma/cm ²) as Hydrogen Electrode at			
	.90	.85	.80	.75 volts
NaBH ₄ -reduced 0.5 mg Pt + 0.5 mg Rh/cm ²	60	120	200	300
Silane-reduced 0.5 mg Pt + 0.5 mg Rh/cm ²	90	170	270	360

EXAMPLE 5

25 The procedure of Example 1 is repeated in every detail except that 2.5 parts of rhodium chloride are substituted for the mixture of noble metal catalysts of Example 4. There is obtained a reduced rhodium metal catalyst which exhibits markedly improved performance characteristics when incorporated in an electrode of a fuel cell.

WHAT WE CLAIM IS:—

35 1. A process for preparing a fuel cell electrode including the step of reducing, in the presence of an electrically conductive filler, a noble metal compound with a di- or tri-substituted silane containing a Si—H group in an alcoholic solvent environment whereby to precipitate on said conductive filler a chemically reduced noble metal having a crystallite size averaging between 20 Å and 35 Å.

45 2. A process according to Claim 1 wherein the reduction is carried out at a temperature of from 20°C. to 100°C.

3. A process according to Claim 1 or Claim 2 wherein the reduction is carried out

in the presence of ethanol or propanol.

4. A process according to any preceding claim wherein the noble metal compound is chloroplatinic acid or rhodium chloride.

5. A process according to any preceding claim wherein the substituted silane is diphenyl silane, triethyl silane, tributyl silane or tribenzylsilane.

6. A process according to any preceding claim including the subsequent steps of adding a binder-waterproofing agent to the conductive filler to form a spreadable paste, and coating a substrate with this paste to form an electrode material.

7. A process for preparing a fuel cell electrode according to Claim 1 and substantially as described in any one of the Examples herein.

8. A fuel cell electrode prepared by a process according to any preceding claim.

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